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INTENSIFICATION OF SINTERING OF MULLITE-CORDIERITE CERAMICS USING MINERALIZERS

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The effect of various mineralizers on the process of sintering of ceramic materials in the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system is investigated. The possibility of decreasing the firing temperature and expanding the firing interval of cordierite-mullite ceramics by using these mineralizers is demonstrated.

Complex ceramic systems are characterized by non-isothermal sintering, and the course of material compaction is determined by the interaction of numerous elementary processes. The problem of activating the sintering process in such systems is quite important. Solving this problem would make it possible to decrease the temperature of ceramic material synthesis and, consequently, the consumption of refractories in ceramic production. Moreover, it is expected that more compact material structures will be obtained, which will improve the mechanical parameters, increase the wear resistance of the articles, and extend their service life.

A comparison of existing physical and chemical methods for activation of sintering [1, 2] revealed advantages of the chemical methods. The chemical methods are based on redox reactions, processes of chemical dissociation of compounds, chemical transfer of material under sintering, etc. Special activators that implement different sintering mechanisms are used for this purpose.

To study activated sintering, we selected ceramic materials based on the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system in the cordierite and mullite crystallization fields. This system is of special interest in the production of insulating ceramics requiring high thermal resistance and sufficient mechanical strength. However, such materials have substantial porosity, which prevents using them in the case of combined action of thermal loads and an aggressive medium, and a firing interval that is relatively narrow [3, 4].

Numerous researchers [3–5] have investigated ways to increase the degree of sintering of cordierite ceramics and expand the sintering interval, employing various mineralizers. Among such mineralizers are alkali-containing mineral rocks, zirconium-bearing materials, glasses of various compositions, etc. The data of these investigations are often contradictory with respect to the effect of the chemical composi-

tion of the forming melt and the temperature dependence of the melt viscosity exerted on the process of sintering and formation of crystalline phases. Furthermore, upon lowering the temperature of synthesis of cordierite materials and expanding the sintering interval, certain thermal and other properties, as a rule, are degraded substantially.

The effect of such active mineralizers as fluorine-bearing components, which manifest a mineralizing action even in small quantities, has not been thoroughly investigated. It is also of interest to study the effect on sintering exerted by additives of alkali-free devitrified glass that is formed from a melt whose composition is similar to the composition of the emerging crystalline phases.

The composition selected for our investigation lies on the line connecting mullite and cordierite in the phase diagram of the ternary system $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ and has the following content (here and elsewhere in wt.-%): 5 MgO , 50 Al_2O_3 , 45 SiO_2 . The raw materials were Veselovskoe refractory clay, raw Onotskii talcum, and technical alumina GN-1.

The mixture was prepared by mixing components of a certain granulometric composition weighed in a prescribed ratio and mineralizing additives. After thorough mixing, the mixture was moistened with water and (or) a carbomethyl cellulose solution to a moisture content of 7–9% and grated through a sieve with a cell size of 1 mm. Molding of the mixture after aging for 1 day was carried out at the pressure of 25 MPa. Sintering was carried out at 1300 or 1200°C (for devitrified glass) in an electric furnace with a 1-h hold at the maximum temperature.

To study the effect of fluorine compounds on the sintering process, sodium silicofluoride, cryolite, and aluminum fluoride were selected. They were introduced into the mixtures in an amount of 0.5–2.0%.

Properties of the samples with the additives that characterize the degree of sintering of the material are given in Table 1. It can be seen that the selected fluorine-containing ad-

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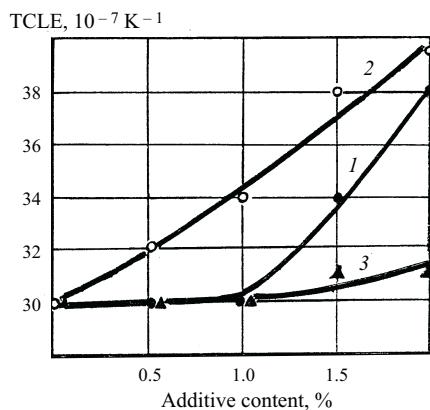


Fig. 1. TCLE of samples as a function of the quantity of the fluorine-containing additives Na_2SiF_6 (1), Na_3AlF_6 (2), and AlF_3 (3).

ditives have an inequivalent effect on the compaction of the system in sintering. Thus, the fire shrinkage, which is the main criterion of compaction, virtually does not change on introducing AlF_3 , whereas the other additives increase this parameter significantly. A correlation of the effect of the indicated additives on other properties of the samples is observed as well. The water absorption of samples with Na_2SiF_6 and Na_3AlF_6 additives decreases from 14 to 6–7%,

TABLE 1

Additive	Weight content, %	Sample properties		
		apparent density, 10^3 kg/m^3	fire shrinkage, %	water absorption, %
Na_2SiF_6	0	1.70	1.8	14.0
	0.5	1.75	2.4	12.0
	1.0	1.85	2.6	11.0
	1.5	1.90	3.0	8.0
	2.0	1.95	3.6	6.0
Na_3AlF_6	0	1.70	1.8	14.0
	0.5	1.80	2.8	11.5
	1.0	1.83	3.3	9.5
	1.5	1.87	3.7	7.5
	2.0	1.94	3.8	7.0
AlF_3	0	1.70	1.8	14.0
	0.5	1.74	1.8	13.5
	1.0	1.74	1.8	13.0
	1.5	1.78	1.9	12.5
	2.0	1.78	2.0	12.5

TABLE 2

Crystalline phase	Interplanar distance of maximum, \AA	Intensity of diffraction maxima		
		initial sample	sample with additive	
		2% Na_2SiF_6	2% Na_3AlF_6	2% AlF_3
Cordierite	3.13	10.0	6.5	8.0
Mullite	2.20	7.5	6.2	7.0
				8.7

and in samples with AlF_3 , it decreases slightly. Accordingly, the apparent density is modified as well. In spite of the small quantity of the fluorine-containing additives introduced, their mineralizing effect in the course of sintering and consolidation of the system is evident. This is due to the fact that fluorine compounds, although they do not increase the total quantity of the melt significantly, foster an increase in the reactivity of the melt by decreasing the melt viscosity and increasing its wetting capacity [6, 7].

The combined action of fluorine and Na^+ cations in introducing Na_2SiF_6 and Na_3AlF_6 activates the sintering process. The alkali-containing cordierite melt is likely to form groups of the type of six-unit rings $[(\text{Si}, \text{Al}) \cdot \text{O}_{18}]^{-12}$ formed with the participation of Na_2O and representing components of the crystalline structure of cordierite. The fluxing action of fluorine in adding AlF_3 is probably compensated by the counteraction of Al^{3+} , which increases the melt viscosity. Consequently, there are reasons to believe that R_2O is a stabilizer for six-unit rings, whose stability in the melt implies a smaller amount of energy consumed on formation of the structure as a whole. The additives introduced ultimately modify the proportion between the crystalline phase, the vitreous phase, and the pores in the material.

An x-ray phase analysis of the samples indicated that the phase composition does not change significantly upon introduction of the additives and is represented by cordierite and mullite. On introducing Na_2SiF_6 and Na_3AlF_6 , the intensity of the diffraction maxima of the crystal phases decreased slightly, which can be accounted for by a certain decrease in their quantity. Cordierite presumably dissolves more easily in the melt than mullite. The diffraction pattern of the sample with AlF_3 exhibited higher diffraction maxima of mullite, compared to the initial sample (Table 2).

A change in the amount of the crystal phases inevitably affected the TCLE of the ceramics. Figure 1 shows the dependence of the TCLE of the samples (in the interval 20–400°C) on the amount of the additives. It can be seen that AlF_3 has virtually no effect on the TCLE, whereas the other two additives increase this coefficient. This is facilitated by the decreased cordierite content and the enrichment of the vitreous phase in sodium and fluorine cations.

Thus, fluorine compounds even in small quantities have an activating effect on the sintering process, especially when introduced in the form of compounds containing alkali metals. Here, the degree of system compaction in sintering is increased significantly, the water absorption is decreased, and the ratio of the structural components, i.e., the crystalline and vitreous phases, is modified, which affects the properties of the material.

We also investigated the effect of devitrified glass, which in crystallization produces similar phases, on the process of sintering of mullite-cordierite ceramics. In this case, the presence of “cybotactic groups” in the melt that are similar in structure to the sintered phase (cordierite) activates sintering. At the same time, the liquid phase can form other crystalline

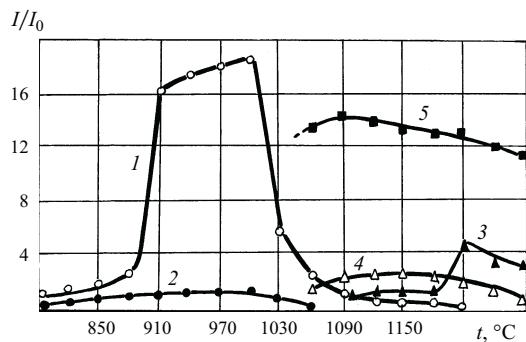


Fig. 2. Relative intensity I/I_0 and sequence of formation of crystalline phases in devitrifying glass in heat treatment: 1) quartz and quartz-like phases; 2) magnesium dititanate; 3) mullite, 4) rutile, 5) cordierite.

phases in the course of the physicochemical reactions, and the sintering process will subsequently proceed mainly in the solid phase. In the stage of sintering, this glass is softened, developing surface-tension forces. In the case where the positions of the initial compositions and the melting point in the phase diagram of the system are close, the indicated structural groups appear in the melt. In the stage of cooling, the glass is devitrified, and the content of the vitreous phase is decreased.

A devitrifying glass whose composition was developed based on the $\text{MgO} - \text{CaO} - \text{SiO}_2 - \text{TiO}_2$ system and is located in the cordierite crystallization field was investigated. Properties of the initial glass and the crystallized devitrified glass are shown in Table 3.

A study of the crystallization of the selected glass under heat treatment (Fig. 2) revealed the following sequence of formation of crystalline phases. Cordierite formation starts at $1050 - 1060^\circ\text{C}$, above which cordierite becomes the dominant crystal phase. At lower temperatures (starting with 880°C), a quartz-like phase is formed, whose quantity sharply decreases after 1000°C and totally disappears by 1180°C . Cordierite is probably formed precisely on the basis of this phase, due to its similar crystal-chemical characteristics. The accompanying phases are rutile, mullite, and, partly, tialite. Thus, the glass crystallization products cannot modify or degrade the phase composition of the sintered ceramics.

The quantity of introduced glass was varied from 4 to 16%. The temperature of mixture sintering was 1200°C . Properties of the material obtained are indicated in Table 4. It can be seen that the glass activates the sintering process (most strongly when the glass content is 10% or more). With the glass content above 12%, the properties virtually do not change. The minimum water absorption is 3.8%, which is significantly lower than in using fluorine-bearing mineralizers.

The effect of the firing temperature on the properties and the phase composition was investigated on samples containing 12% devitrifying glass (Fig. 3). The consolidation process starts to develop actively only after 1100°C , when substantial softening of the glass takes place, the amount of melt

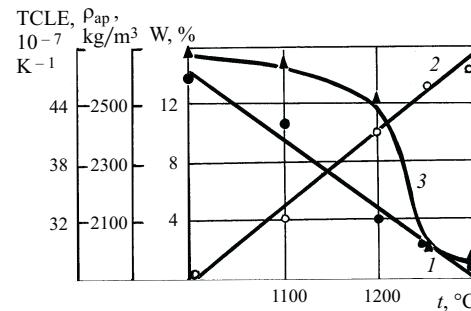


Fig. 3. Effect of the firing temperature on the properties of samples with a constant additive (12%) of devitrifying glass: 1) water absorption W ; 2) apparent density ρ_{ap} ; 3) TCLE.

increases, and surface-tension forces arise. At the same time, the diffusion process arises in the solid phase. The combination of these processes results in substantial compaction of the material. The water absorption decreases to 1%, which is true in a temperature interval of at least 50°C , which is very important for this type of ceramics with a very narrow interval of the sintered state. The expansion of the sintering interval can be attributed to the introduction of alkali-free high-alumina glass that has a high softening temperature and a high viscosity in melting. The viscosity of the alkali-free melt decreases less intensely with increasing temperature than that of alkali glasses. Therefore, such a melt facilitates sintering in a wider temperature interval without signs of overburning.

As the sintering temperature is increased, the TCLE of the samples first increases slightly, and then it decreases sharply to $(20 - 30) \times 10^{-7} \text{ K}^{-1}$ in the interval of $1150 - 1200^\circ\text{C}$, which is evidence of substantial modification of the

TABLE 3

Parameter	Glass	
	initial	crystallized
Density, kg/m^3	2450	2670
Microhardness, MPa	5600	9050
TCLE, 10^{-7} K^{-1}	41.5	17.1
Softening temperature, $^\circ\text{C}$	980 - 1000	1300
Bending strength, MPa	7.8	15.0

TABLE 4

Weight content of additive, %	Sample properties		
	density, %	apparent density, 10^3 kg/m^3	water absorption, %
0	27.0	1.80	14.0
4	22.5	1.90	12.0
8	14.0	1.95	11.0
12	8.0	2.40	4.0
16	5.0	2.45	3.0

structure. In the case of introduction of glass, the TCLE not only does not increase but even decreases to some extent, compared to the initial composition. The mineralizing agents investigated previously had a substantial negative effect on this parameter. In this case, some of the vitreous phase crystallizes, forming an additional amount of cordierite. The phase composition virtually does not change, and the main crystalline phases are cordierite and mullite. As the quantity of glass increases, the formation of mullite becomes somewhat less intense.

Thus, use of devitrifying glass in sintering of mullite-cordierite ceramics makes it possible to obtain a low-porosity material at a firing temperature of 1200°C, which is caused by the increased viscosity of the alkali-free melt and the presence of active "cybotaxic groups" that are similar in structure to the sintered phase.

Technological parameters for producing articles from powdered mixtures in accordance with ceramics technology have been developed for the optimum composition containing 12% devitrified glass. An experimental lot of insulating refractory bushings was manufactured. The products were tested successfully as a lining in induction generators at a number of machine-building companies in Belarus. The service life of the articles was increased 10-fold or more, compared to chamotte articles currently used. This makes it pos-

sible to recommend these materials for heat and electric insulators, structural parts in machine-building, metallurgy, and chemical and other sectors of industry.

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